Fundamentals of a Solar-thermal Mn_2O_3/MnO Thermochemical Cycle to Split Water

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Overview

Timeline

- Start: 6-1-2005
- End: 5-31-2009
- 40% Complete

Budget

•**Total Project Funding**

$410,000 DOE ($180,00 via UNLV)

$102,500 Cost share

•**Funds received in FY06**

$ 80,000

Barriers

- **AU. High-Temperature Thermochemical Technology**
- **AV. High-Temperature Robust Materials**
- **AW. Concentrated Solar Energy Capital Cost**
- **AX. Coupling Concentrated Solar Energy and Thermochemical cycles**

Partners

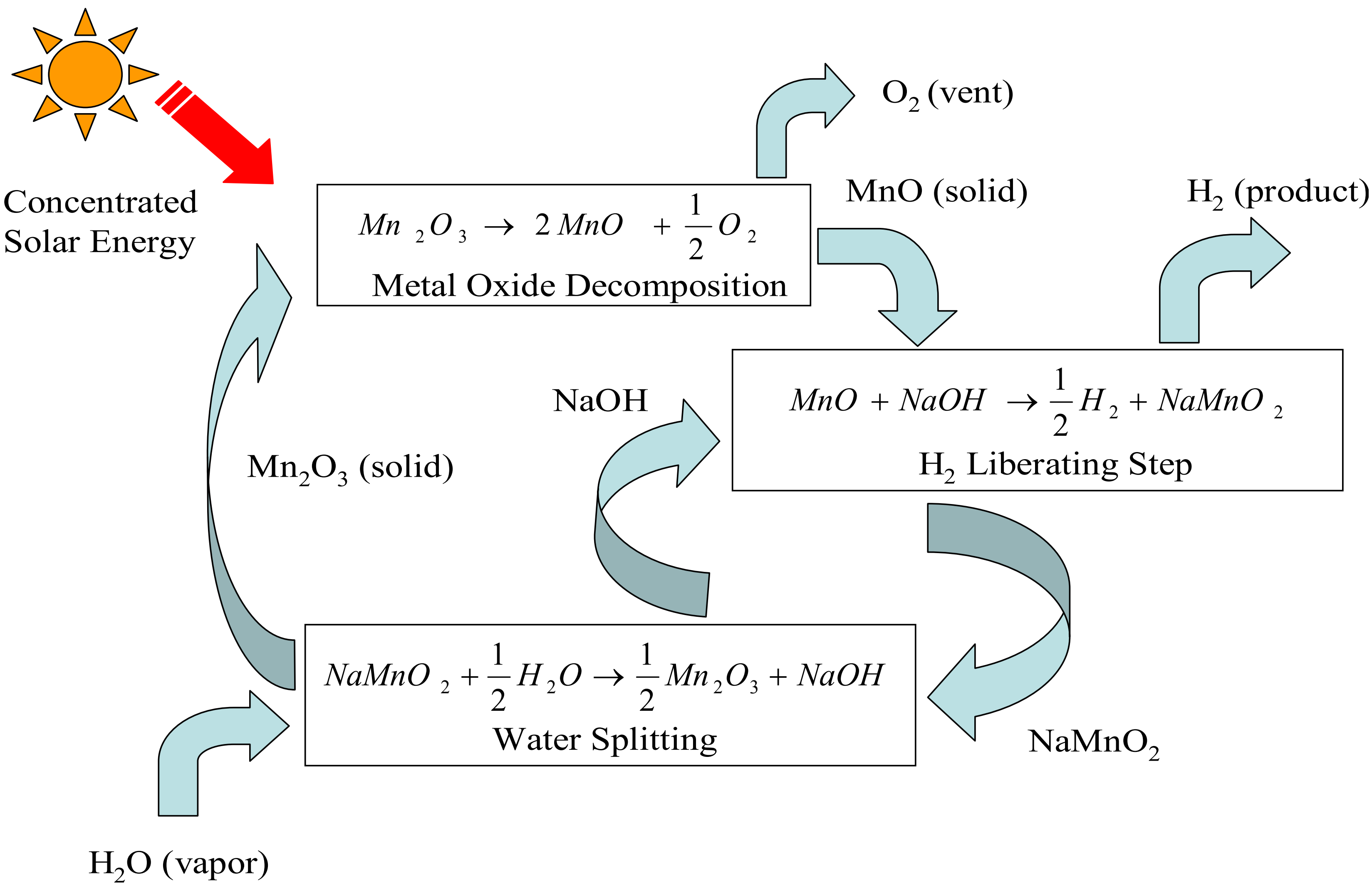
Swiss Federal Institute of Technology

University of Nevada – Las Vegas

Objectives

- Research and develop a cost effective Mn_2O_3/MnO solar-thermal thermochemical cycle through theoretical and experimental investigation
- Based on the above, develop a process flow diagram and carry out an economic analysis of the best process option

Literature Cycle



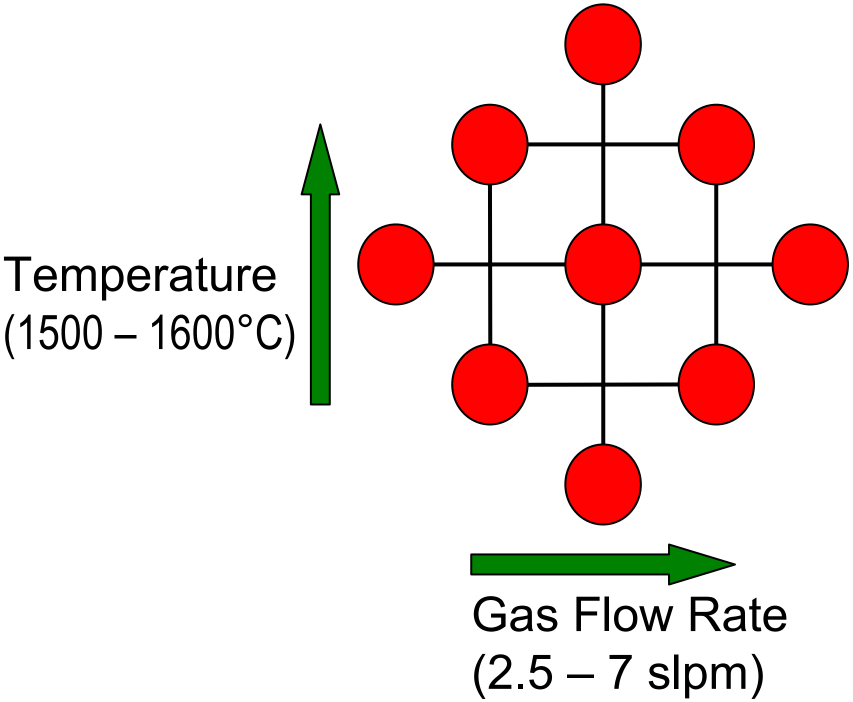
Approach

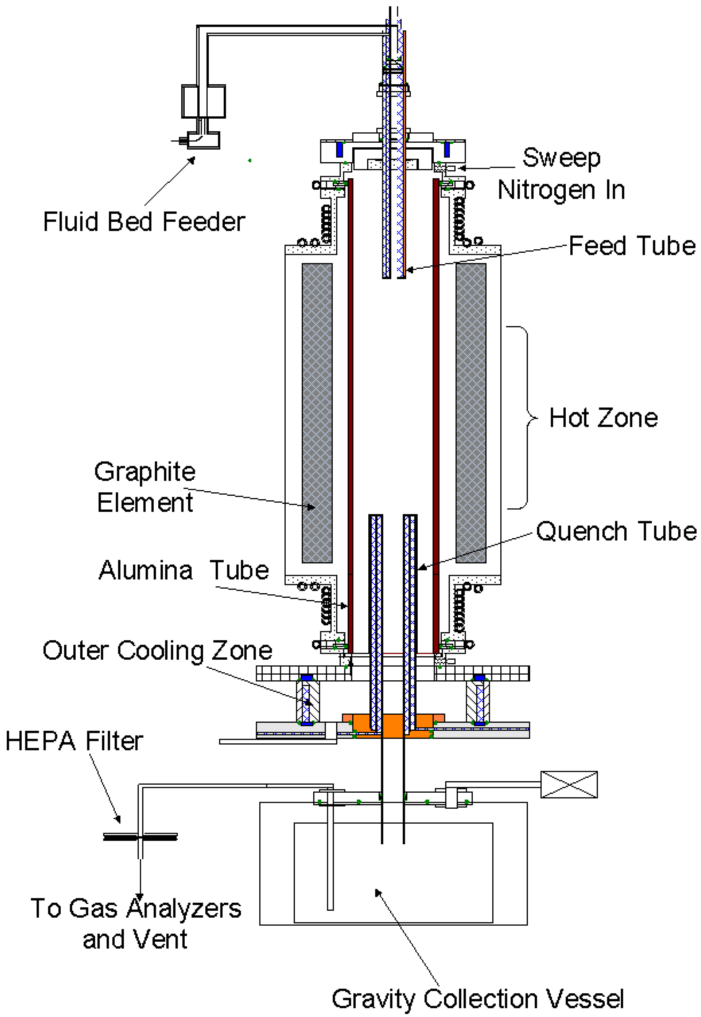
- Thermodynamic assessment of the cycle
- Experimental investigation
  - Investigate Mn_2O_3 dissociation and mechanism
  - Investigate H_2 generating step
  - Investigate ways in which to recover NaOH after H_2 generating step
  - Develop alternative methods in which to close the cycle
- Use H2A framework to economically evaluate the cycle

Technical Accomplishments / Progress / Results

- Demonstrated high conversions of Mn_2O_3 dissociation in an Aerosol Flow Reactor (AFR)
- NaOH removal by vaporization was investigated
- Explored carrying residual $NaMnO_2$ through the cycle
- Testing in progress with mixed manganese oxides for more efficient NaOH recovery

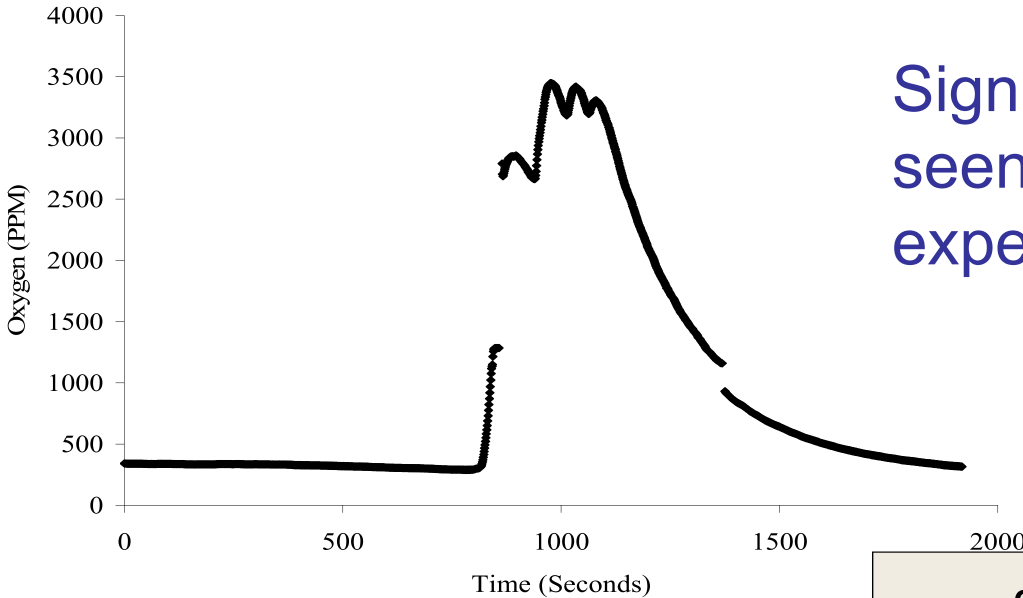
Mn_2O_3 Dissociation





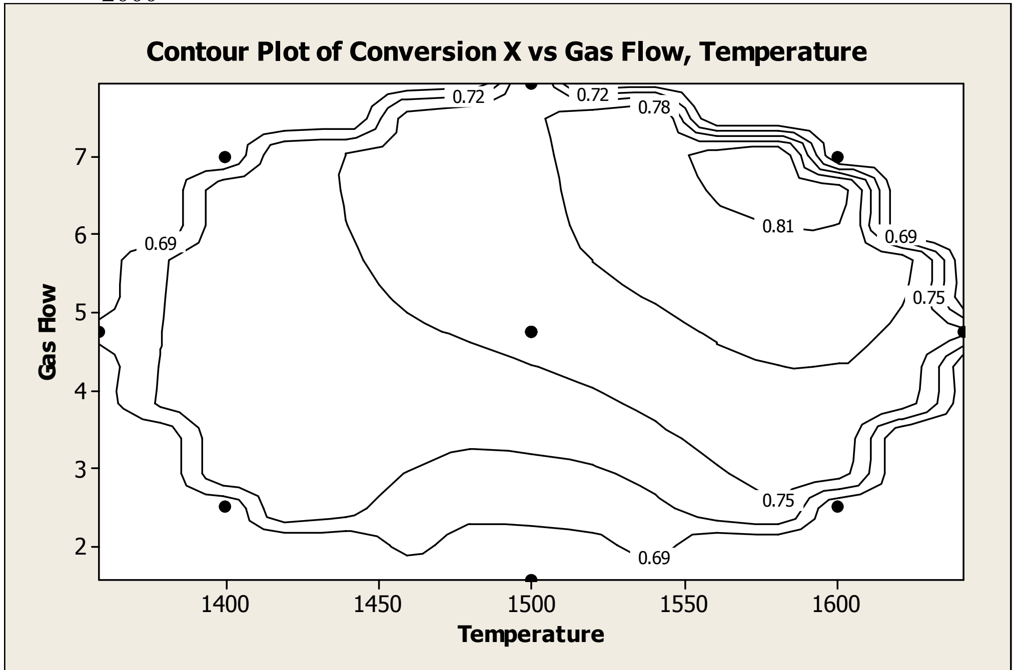
Experiments are being conducted with a two factor Central Composite Design (CCD)

Mn_2O_3 Dissociation Results

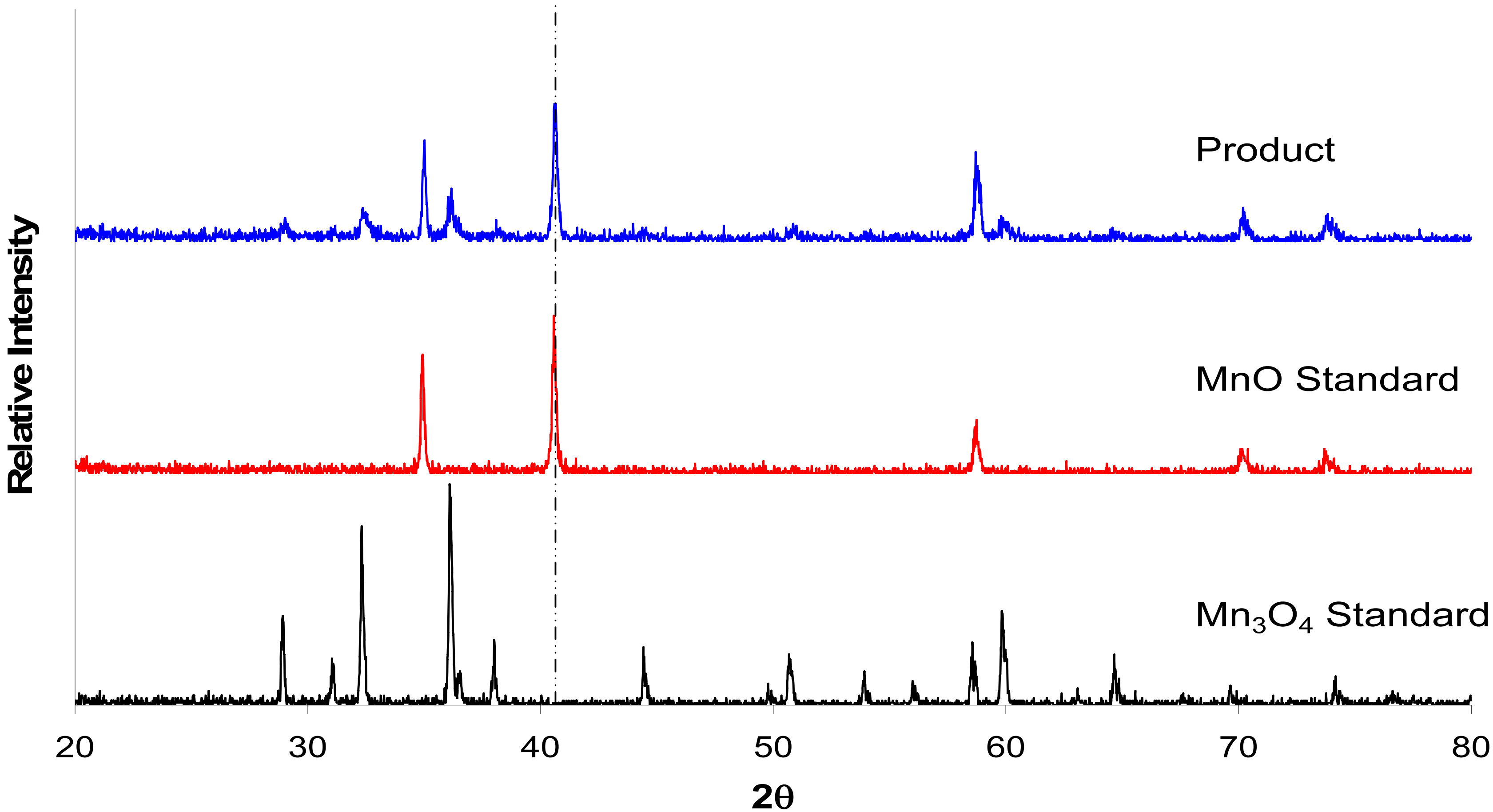


Significant oxygen generation is seen in situ during a typical experimental run

Results show increasing temperature and gas flow rate resulted in the highest conversion. This indicates that recombination of oxygen may have a significant effect.



XRD Spectra



XRD spectra show a strong MnO spectrum and a weak Mn_3O_4 spectrum. A dotted line helps illustrate that all of the peaks can be seen from the MnO standard and only the major peaks from the Mn_3O_4 standard.

Dissociation Objective Progress

- Demonstrated high conversions in an AFR
  - Oxygen generation detected in situ
  - XRD confirmed MnO presence
  - O_2 analysis showed conversions as high as 82%

- More experimental work to come
  - Investigation of recombination rates
  - Thermogravimetric mechanistic studies

Steps 2 - 3 in Manganese Cycle

- NaOH separation is the biggest challenge
  - 10% sodium residual
  - 100 torr H_2
- Solutions – Currently investigating
  - Thermal separation of NaOH
  - Processing residual $NaMnO_2$
  - Mixed manganese oxides
- More Potential Solutions
  - Different M-OH sources (Potassium, …)
  - Different separation approaches

Thermal Separation of NaOH

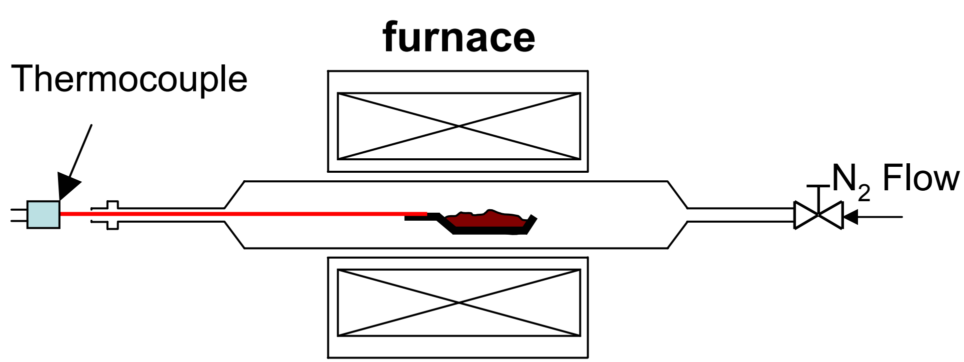
Vaporize NaOH to separate it from Mn_2O_3

- 2_{III}^{5-2} screening design

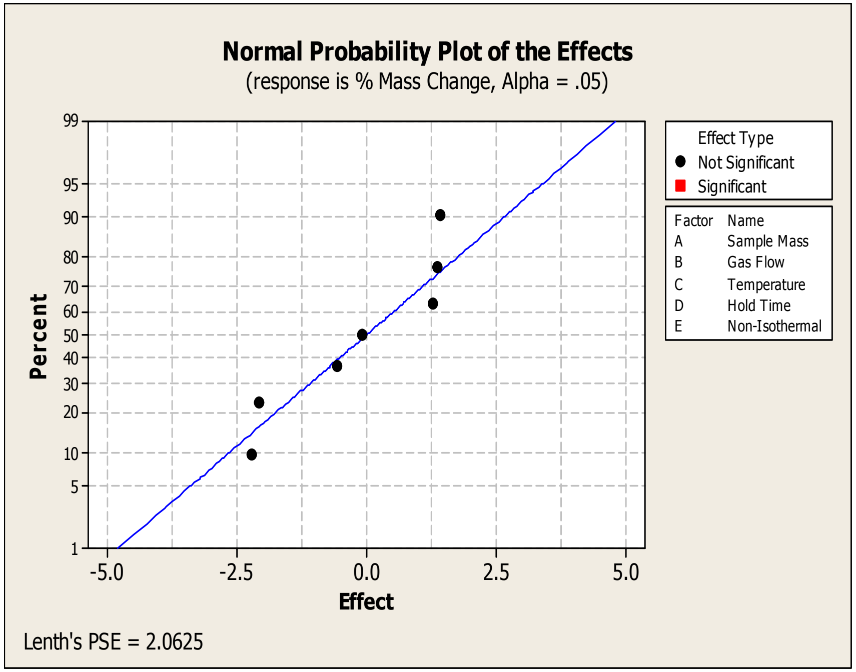
Factors		
Sample Mass	Non-Isothermal/Isothermal	
Gas Flow Rate	Temperature	Hold Time

A horizontal tube furnace is utilized to conduct experiments

- Pull sample into hot zone at desired temperature and time



NaOH Vaporization Results



Results indicate that a significant amount of NaOH was not vaporized. In addition, a statistical analysis shows that there are no significant effects. This indicates that within the ideal operating ranges selected for the factors that it is not possible to achieve a high vaporization rate of NaOH.

For the vaporization to proceed at an ideal rate a high temperature is required

- **Likely problems with a higher temperature**
  - Reverse reaction to $NaMnO_2$
  - Partial reduction of Mn_2O_3 to Mn_3O_4

Conclusion: Vaporization of NaOH is not a viable method to separate Mn_2O_3 and NaOH

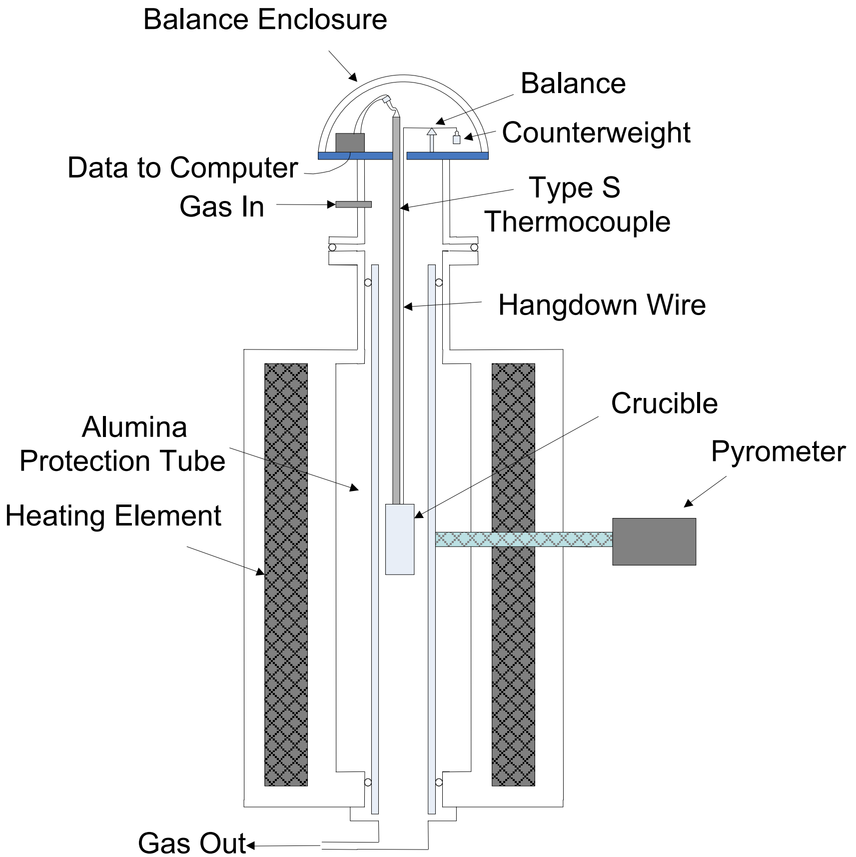
Processing Residual $NaMnO_2$

High temperature step with $NaMnO_2$

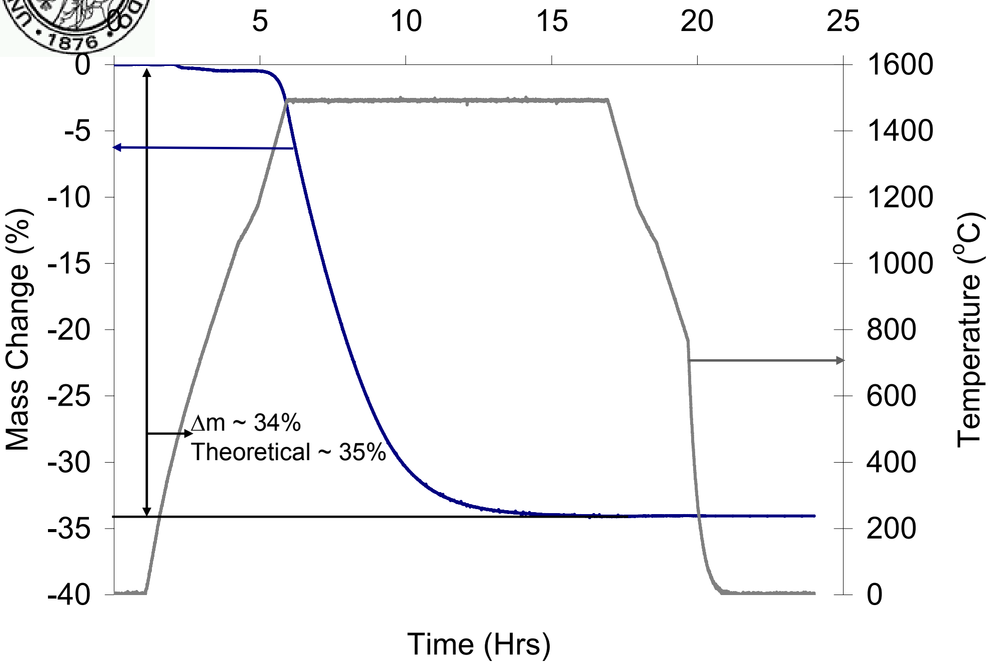
$2NaMnO_2(s) \rightarrow Na_2O(vapor) + 2MnO(s) + \frac{1}{2}O_2$

$Na_2O + H_2O \rightarrow 2NaOH$

- Attempt proof of concept at Mn_2O_3 dissociation operating conditions
  - Use a Thermal Gravimetric Analyzer (TGA)



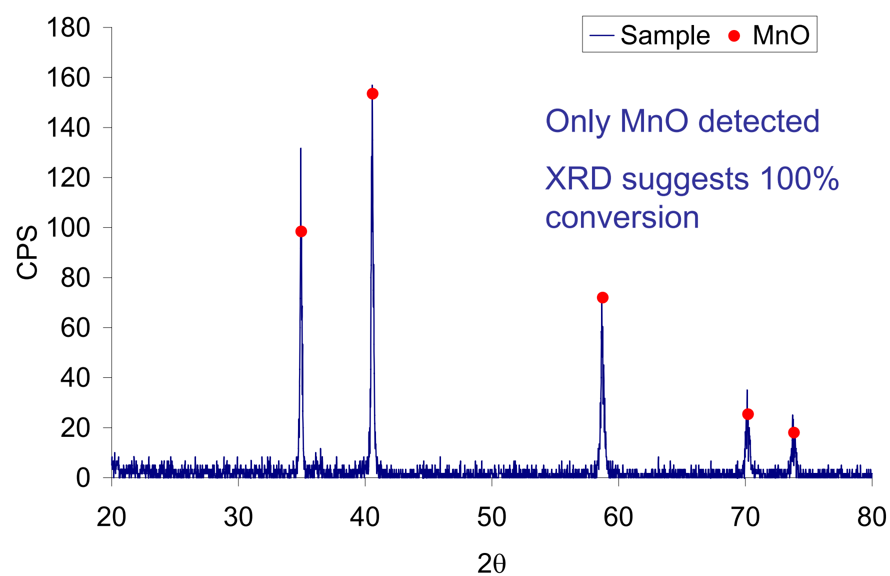
Proof of Concept Results



It has been demonstrated using a TGA that MnO is formed at 1500°C

- What form does the sodium take?
- Will the reaction kinetics become faster when diffusion resistances are negligible?

- Future work
  - Study sodium product gas with a mass spectrometer
  - Look at reactions kinetics in an AFR



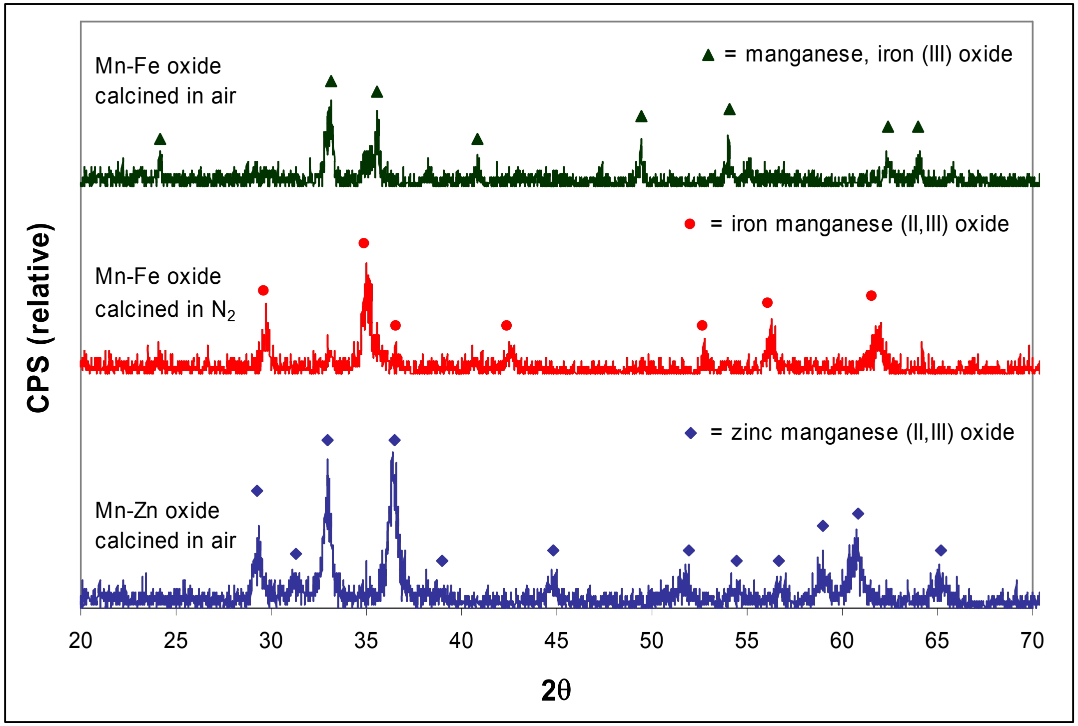
Mixed Manganese Oxides

Use of mixed metal oxides may potentially improve Mn_2O_3/NaOH separation

- Research divided into 3 phases
  1. Synthesize $Mn_xFe_{1-x}O$ and $Mn_xZn_{1-x}O$
  2. Verify hydrogen production with these mixed oxides

     $Mn_xFe_{1-x}O + NaOH \rightarrow ?\ NaMn_xFe_{1-x}O_2 + ½H$
  3. Investigate the mixed oxide – NaOH separation efficiency
     - Compare with Mn_2O_3 - NaOH separation

Mixed Oxide Identification



Sol-gel precipitation reaction in basic solution from metal salts

- Calcination of precipitate (air, N2)

Currently mixed manganese oxides are showing mixed oxidation states. It is necessary to produce these with only the +2 oxidation state

Next steps

- Calcine with reducing atmosphere
- Reduce existing mixed oxide into lower oxidation state
  - This will verify hydrogen production

Future Work

- On sun testing of Mn_2O_3 dissociation
  - Reactor design and construction
  - Materials testing
    - Alumina
    - Silicon Carbide
- Continue future work plans detailed earlier in the presentation
  - Mn_2O_3 decomposition
  - Processing residual $NaMnO_2$
  - Mixed manganese oxide investigation
- Update H2A analysis with new experimental results

Conclusions/Summary

Significant experimental progress has been made with the Mn_2O_3/MnO cycle

- High conversions for Mn_2O_3 have been demonstrated
- Potential solutions for NaOH recovery have been identified and investigations have begun
- Studies in alternative ways to close the cycle are ongoing
  - Mixed manganese oxides